

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED / ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER P67142US0
		US APPLICATION NO. (if none, see PCT/PTO Form 1) 097926184
INTERNATIONAL APPLICATION NO. PCT/EP00/02424	INTERNATIONAL FILING DATE 18 March 2000	PRIORITY DATE CLAIMED 25 March 1999
TITLE OF INVENTION A METHOD FOR THE PREPARATION OF SELF-CLEANING REMOVABLE SURFACES		
APPLICANT(S) FOR DO/EO/US Wilhelm BARTHOLOTT and Christoph NEINHUIS		

Applicant herein submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for Internatl. Preliminary Examination was made by the 19th month from earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the Internatl. Preliminary Examination report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

International Search Report - EPO
 PCT/IB/304 Form
 PCT/IB/306 Form
 PCT/IB/308 Form
 First Page of Publication
 International Preliminary Examination Report - with no annexes

US APPLICATION NO (if known, see 37 CFR 1.5) <div style="font-size: 2em; font-weight: bold;">09/926184</div>		INTERNATIONAL APPLICATION NO <div style="font-weight: bold;">PCT/EP00/02424</div>		ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold;">P67142US0</div>	
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17. <input checked="" type="checkbox"/> The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): Internatl. prelim. examination fee paid to USPTO (37 CFR 1.492 (a) (1)) .. \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (2)) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) .. \$710.00 Neither international preliminary examination fee (37 CFR 1.492 (a) (3)) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO) \$1000.00 International preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (4)) and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00 Search Report prepared by the EPO or JPO (37 CFR 1.492 (a) (5)) \$860.00 <div style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>				CALCULATIONS		PTO USE ONLY	
				\$ 860.00			

Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 130.00			
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Claims	Number Filed	Number Extra	Rate		
Total Claims	10 - 20 =	-0-	x \$18.00	\$	
Independent Claims	3 - 3 =	-0-	x \$80.00	\$	
Multiple Dependent Claim(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 990.00	
Reduction by 1/2 for filing by small entity , if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$ 990.00	

Processing fee of \$130 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f))				\$			
TOTAL NATIONAL FEE =				\$ 990.00			
Fee of \$40.00 for recording the enclosed assignment (37 CFR 1.21(h)). Assignment must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31).				\$			
TOTAL FEES ENCLOSED =				\$ 990.00			

				Amt. to be refunded:		\$	
				Amt. charged:		\$	

a. ☒ A check in the amount of \$ 990.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 06-1358 in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge my account any additional fees set forth in §1.492 during the pendency of this application, or credit any overpayment to Deposit Account No. 06-1358. A duplicate copy of this sheet is enclosed.

SEND ALL CORRESPONDENCE TO:

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By

William E. Player
 Reg. No. 31,409

JPH&S 3/95

09/926184

JCO3 Rec'd PCT-TO 20 SEP 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Wilhelm BARTHLOTT et al.

Serial No.: New

Filing Date: September 20, 2001

For: A METHOD FOR THE PREPARATION OF SELF-CLEANING
REMOVABLE SURFACES

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified application as follows:

IN THE SPECIFICATION

On ~~page~~ 1, immediately following the title, please insert the following sentence: --This is a nationalization of PCT/EP00/02424 filed March 18, 2000 and published in German.--

IN THE CLAIMS

Please amend claims 5 and 7 as follows:

5. (amended) The method according to claim 1, characterized in that said application of the solution, dispersion or emulsion is effected by spraying.

7. (amended) The method according to claim 1, characterized in that said hydrophobic material is additionally oleophobic.

09/926184

REMARKS

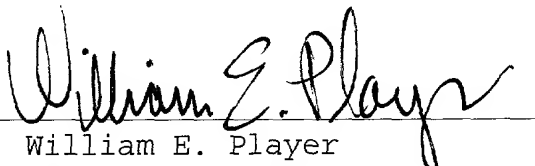
The foregoing Preliminary Amendment is requested in order to delete the multiple dependent claims and avoid paying the multiple dependent claims fee.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

Early action on the merits is respectfully requested.

Respectfully submitted,

JACOBSON HOLMAN PLLC

By 
William E. Player
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Atty. Docket: P67142US0
Date: September 20, 2001
WEP/cmf

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS

5. (amended) The method according to claim 1 [at least one of claims 1 to 4], characterized in that said application of the solution, dispersion or emulsion is effected by spraying.

7. (amended) The method according to claim 1 [at least one of claims 1 to 6], characterized in that said hydrophobic material is additionally oleophobic.

SMB

A Method for the Preparation of Self-Cleaning Removable Surfaces

The present invention relates to a method for the preparation of self-cleaning surfaces.

The cleaning of the surfaces of objects is of considerable technical and economical importance, in part for optical and aesthetical reasons, and in part for technical reasons, especially if the surfaces are light-transmitting surfaces which must be cleaned from time to time for maintaining their function.

Many attempts have been made to create technical surfaces which are soil-repellent and/or self-cleaning. The manufacturers of polymer films or polymer sheets have tried to solve this problem by producing as smooth as possible surfaces and rendering those surfaces either extremely hydrophobic or extremely hydrophilic. Examples thereof include surfaces made of the extremely hydrophobic Teflon or the extremely hydrophilic "no-drop coatings" from which water and soil can flow off without forming drops.

CH-PS-26 82 58 describes water-repellent surfaces which exhibit a contact angle with water of more than 120° . They are obtained by applying powders, such as china clay, talcum, clay or silica gel, to a substrate, the powder being preliminarily hydrophobized by organic silicon compounds. The application is performed together with curable resins, or from solutions with organic solvents. Permanently hydrophobic surfaces cannot be prepared in this way. Also, no indications are found as to the grain sizes or grain size distribution of the powders. The properties of the surfaces thus obtained are compared with those of the leaves of nasturtium. In this comparison, it has to be noted that it had been neither known nor technically analyzable whereupon the properties of the leaf surface of nasturtium are

based. Recently performed examinations have shown that nasturtium has an extremely fine ultrastructure with structural elements smaller than 2 μm .

US-P-3,354,022 describes a water-repellent surface having protrusions and recesses and an air content of at least 60% for which a surface contact angle of more than 90° is found.

DE-PS-10 23 217 describes a mold for the preparation of molded parts having a rough surface. The mold is to serve for the preparation of molded parts made of rubber or plastic having a rough surface. Thus, the walls of the mold are coated with coarse corundum powder and a stoving paint. The molds yield products having occasional recesses and hence improved adhesive properties. The usual vulcanization skin is even avoided. For example, the surfaces thus obtained are readily inscribed. Thus, the products are surely not self-cleaning with moving water.

JP-A-62-191447 describes a method for increasing the water-repellency of a surface. Thus, a plasma polymer film is applied, roughened by etching, and then a second plasma polymer film is applied.

JP-A-3-174279 (Abstract) describes a method for the preparation of matt decorative surfaces on sheets or films. They are prepared using paints which are partially cured by ionizing radiation and in which unspecified patterns are impressed in an unspecified way. Curing is then completed by further irradiation.

Applicant's extensive examinations have provided the surprising result that it is technically possible to artificially render the surfaces of objects self-cleaning by providing them with an artificial surface structure of protrusions and recesses, wherein care has to be taken that the distance between said protrusions of the surface structure is in a range of from 0.1 to 200 μm , preferably from 0.1 to 100 μm , and the height of said protrusions is in a range of from 0.1 to 100 μm , preferably from 0.1 to 50 μm , and care has to be taken that said protrusions consist of hydrophobic polymers or permanently hydrophobized materials, and

care is taken that said protrusions cannot be removed by water or water with detergents (cf. WO 96/04123).

It has been the object of the present invention to provide a method for the preparation of self-cleaning surfaces which can be removed with detergent solutions. This object is achieved by a method having the features of claim 1.

The method according to the invention for the preparation of self-cleaning surfaces having protrusions and recesses, wherein the distance between said protrusions is in a range of from 0.1 to 200 μm and the height of said protrusions is in a range of from 0.1 to 100 μm , is based on the application of a hydrophobic material which forms a self-cleaning surface by self-organization when the solvent is evaporated to a surface followed by drying, wherein the material applied can be removed with aqueous detergent solutions. The hydrophobic material may be in the form of a solution, dispersion or emulsion.

"Removable by detergents" means that the material applied can be removed by the action of aqueous detergent solutions, at least upon prolonged action, by dissolving at least parts of the material applied. Such materials applied according to the invention can also be removed mechanically, for example, by brushing, scratching or high-pressure cleaning with water.

In one embodiment, the hydrophobic material is a wax which forms a microstructured self-cleaning surface by self-organization.

In another embodiment, the solution, dispersion or emulsion contains solid particles. These may be themselves hydrophobic or hydrophilic when employed together with hydrophobic materials, such as waxes.

The application of the hydrophobic material may be effected by spraying, for example, using a spray can or a spray gun. Depending on the kind of the intended application, it may be advantageous for the hydrophobic material to be additionally oleophobic.

It is also possible to transport the hydrophobic material through a vapor-permeable surface by co-transportation with water.

The hydrophobic materials suitable for the method according to the invention include, in particular, longer-chain secondary alcohols and alkanediols, β -diketones, secondary ketones and long-chain alkanes. Particularly suitable are nonacosane-10-ol, nonacosane-7,10-diol, nonacosane-5,10-diol, hentriacontane-12,14-dione, hentriacontane-8,10-dione, palmitone and other hydrophobic substances which are soluble in volatile solvents and form a hydrophobic water-repellent surface by self-organization when these solvents are evaporated.

Of particular technical importance are self-cleaning surfaces of objects which are light-transmitting and which are to maintain their light-transmission for a long period of time for optical, aesthetical or technical reasons. In particular, the objects include light-transmitting glass-work on buildings, vehicles, solar collectors etc. The removability of the hydrophobic material is of advantage, in particular, when the self-cleaning properties are needed only temporarily, for example, during storage or shipping, but are otherwise undesirable, for example, for aesthetic reasons.

Also of economical and technical importance, however, is the preparation of self-cleaning surfaces for house facades, roofs, monuments and tents, and for interior coatings of silos, tanks or pipelines which either contain aqueous solutions or are readily cleaned without residues by moving water. The outer coatings of vehicles such as cars, trains or airplanes are also of interest.

Optimum results are achieved if the protrusions of the surface structures are close enough to one another to avoid contact of the recesses present between the protrusions with drops of water. If the protrusions of the surface structures are too close to one another or if the recesses are not profound enough, they again act as a closed surface and thus can be better wetted. Therefore, it should be sought that the height of the protrusions above the ground increase as the distance between the protrusions increases. The measurements performed so far have shown that good results are achieved within the claimed limits for the distances and heights of

the protrusions. Surfaces having protrusions of from 0.1 to 50 μm for which the distance between the protrusions is from 0.1 to 100 μm yield optimum results.

The invention is further illustrated by the following Examples.

Example 1:

Hentriacontane-14,16-dione as a 0.1% solution in hexane or ethyl acetate is sprayed onto an arbitrarily selected surface using a spray can or spray gun. While the solvent evaporates, the hentriacontane-14,16-dione forms crystals in the form of small tubes by self-organization, the majority of which have a diameter of 0.2 μm and a length of from 0.5 to 5 μm . This coating renders a wettable surface hydrophobic, and the contact angle is increased up to 160°. From such surfaces, contaminating particles are washed off by moving water, wherein the coating itself is also removed on a long-term basis. To increase the roughness of the coating, a hydrophilic (e.g., quartz powder) or hydrophobic powder (e.g., Teflon) can be admixed with the solution.

Example 2:

Commercially available gypsum is mixed with water and a silicate (Wacker BS 15) at a ratio of 1:10:2 (weight percent), followed by applying it with a paintbrush or roll. Drying up forms a microrough surface whose structure is determined by the acicular crystals of the gypsum. After the water has evaporated, these are covered by a layer of the hydrophobizing agent. The contact angles on such a surface are above 150°.

Example 3:

Commercially available gypsum is mixed with water and a silicate (Wacker Silikon WI) at a ratio of 1:10:0.5 (weight percent), followed by applying it with a spray gun. Drying up forms a microrough surface whose structure is determined by the acicular crystals of the gypsum. After the water has evaporated, these are

covered by a layer of the hydrophobizing agent. The contact angles on such a surface are above 150° .

Example 4:

A water-vapor-permeable polymer (e.g., polyurethane) is coated on one side thereof with a waxy substance (e.g., hentriacontane-14,16-dione) which is characterized by a capability of structure formation (see Example 1). If water is allowed to diffuse through the polymer, the wax is cotransported and forms the desired microstructures on the surface.

In this system, by using a sufficiently high amount of wax, a certain sustained effect can be achieved because damaged or eroded structures can be regenerated for some time.

CLAIMS:

1. A method for the preparation of self-cleaning surfaces having protrusions and recesses, wherein the distance between said protrusions is in a range of from 0.1 to 200 μm and the height of said protrusions is in a range of from 0.1 to 100 μm , by applying a solution, dispersion or emulsion containing a hydrophobic material which forms a self-cleaning surface by self-organization when the solvent is evaporated, followed by drying, wherein the material applied can be removed with detergents.
2. The method according to claim 1, characterized in that said hydrophobic material is a wax.
3. The method according to claim 1, characterized in that said hydrophobic material comprises waxy substances, such as primary or secondary alcohols and alkanediols, β -diketones, secondary ketones and long-chain alkanes.
4. The method according to claim 1, characterized in that said solution, dispersion or emulsion contains solid particles.
5. The method according to at least one of claims 1 to 4, characterized in that said application of the solution, dispersion or emulsion is effected by spraying.
6. The method according to claim 5, characterized in that said application is effected using a spray can or spray gun.
7. The method according to at least one of claims 1 to 6, characterized in that said hydrophobic material is additionally oleophobic.
8. An object with a surface having protrusions and recesses, wherein the distance between said protrusions is in a range of from 0.1 to 200 μm and the height of said protrusions is in a range of from 0.1 to 100 μm , wherein

[illegible]

9. Use of secondary alcohols and alkanediols, β -diketones, secondary ketones and long-chain alkanes as a hydrophobic material for the preparation of self-cleaning surfaces.
10. The use according to claim 9, characterized in that nonacosane-10-ol, nonacosane-7,10-diol, nonacosane-5,10-diol, hentriacontane-12,14-dione, hentriacontane-8,10-dione or palmitone is used as said hydrophobic material.

DECLARATION
AND POWER OF ATTORNEY
U.S.A.

ALL PATENTS, INCLUDING DESIGN
FOR APPLICATION BASED ON PCT; PARIS CONVENTION,
NON PRIORITY; OR PROVISIONAL APPLICATIONS

FOR ATTORNEYS' USE ONLY

ATTORNEYS' DOCKET NO.

P67142US0

As a below named inventor, I declare that my residence, post office address and citizenship are stated below next to my name, the information given herein is true, that I believe that I am the original, first and sole inventor (if only one name is listed at 201 below), or an original, first and joint inventor (if plural inventors are named below at 201-203, or on additional sheets attached hereto) of the subject matter which is claimed and for which patent is sought on the invention entitled:

A METHOD FOR THE PREPARATION OF SELF-CLEANING REMOVABLE SURFACES

which is described and claimed in: ☒ PCT International Application No. PCT/EP00/02424 filed March 18, 2000
☐ the attached specification ☒ the specification in application Serial No. _____ filed September 20, 2001
(if applicable) and amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.
I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)	Priority Claimed
<u>199 13 602.5</u> <u>GERMANY</u> <u>25 March 1999</u>	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____ (Number) (Country) (Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____ (Number) (Country) (Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date	Application No.	Filing Date
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Application Serial No.)	_____ (Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status: patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status: patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys (Registration No.) to prosecute this application, receive and act on instructions from my agent, and transact all business in the Patent and Trademark Office connected therewith. HARVEY B. JACOBSON, JR. (20,851); JOHN CLARKE HOLMAN (22,769); MARVIN R. STERN (20,640); ALLEN S. MELSER (27,215); MICHAEL R. SLOBASKY (26,421); JONATHAN L. SCHERER (29,851); IRWIN M. AISENBERG (19,007); WILLIAM E. PLAYER (31,409); YOON S. HAM (45,307) and NATHANIEL A. HUMPHRIES (22,772)

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PROFESSIONAL LIMITED LIABILITY COMPANY

*Inventor(s) name must include at least one unabbreviated first or middle name.

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201	RESIDENCE & CITIZENSHIP	<u>BARTHOLOTT</u>	<u>Wilhelm</u>	
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202	FULL NAME * OF INVENTOR	<u>NEINHUIS</u>	<u>Christoph</u>	
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			<u>GERMANY</u>	<u>D-53117</u>
203	FULL NAME * OF INVENTOR			
	RESIDENCE & CITIZENSHIP			
	POST OFFICE ADDRESS			

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201*	SIGNATURE OF INVENTOR 202*	SIGNATURE OF INVENTOR 203*
<u>X</u> <u>W. Bartholott</u>	<u>X</u> <u>C. Neinhuis</u>	
DATE <u>5-Oct-01</u>	DATE <u>5.10.2001</u>	DATE

☐ Additional inventors are named on separately numbered sheets attached hereto.